

Photoinduced Absorption Spectra of Halogen-Bridged Binuclear Metal Complexes: Possible Contrast between $R_4[\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4X] \cdot n\text{H}_2\text{O}$ and $\text{Pt}_2(\text{CH}_3\text{CS}_2)_4\text{I}$

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The optical conductivity of photogenerated solitons in quasi-one-dimensional halogen-bridged binuclear metal (*MMX*) complexes is investigated with particular emphasis on a comparison between the two family compounds $R_4[\text{Pt}_2(\text{pop})_4X] \cdot n\text{H}_2\text{O}$ ($X = \text{Cl}, \text{Br}, \text{I}$; $R = \text{NH}_4, \text{Na}, \text{K}, \dots$; $\text{pop} = \text{diphosphonate} = \text{P}_2\text{O}_5\text{H}_2^{2-}$) and $\text{Pt}_2(\text{dta})_4\text{I}$ ($\text{dta} = \text{dithioacetate} = \text{CH}_3\text{CS}_2^-$). Soliton-induced absorption spectra for the *pop* complexes should split into two bands, while those for the *dta* complex should consist of a single band.

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Quasi-one-dimensional halogen (X)-bridged metal (M) complexes [1,2], which are referred to as *MX* chains, provide an interesting stage [3–5] performed by electron-electron correlation, electron-lattice interaction and low dimensionality. The Mott and Peierls insulators compete with each other in their ground states [6,7], while their photoexcited states exhibit novel decay kinetics [8,9]. A large choice of metals, bridging halogens, ligand molecules and counter ions enables us to investigate electron-phonon cooperative phenomena in the one-dimensional Peierls-Hubbard system systematically [10].

In recent years, binuclear metal analogs which are referred to as *MMX* chains have stimulated renewed interest in this system, exhibiting a wider variety of ground states [11–17]. The existent *MMX* compounds consist of two families: $R_4[\text{Pt}_2(\text{pop})_4X] \cdot n\text{H}_2\text{O}$ ($X = \text{Cl}, \text{Br}, \text{I}$; $R = \text{NH}_4, \text{Na}, \text{K}, \dots$; $\text{pop} = \text{diphosphonate} = \text{P}_2\text{O}_5\text{H}_2^{2-}$) [18,19] and $M_2(\text{dta})_4\text{I}$ ($M = \text{Pt}, \text{Ni}$; $\text{dta} = \text{dithioacetate} = \text{CH}_3\text{CS}_2^-$) [20,21]. The former compounds structurally resemble conventional *MX* ones and generally exhibit the same type of mixed-valent ground state with halogen-sublattice dimerization [22,23]: $\dots X^- \dots \text{Pt}^{2+} \text{Pt}^{2+} \dots X^- - \text{Pt}^{3+} \text{Pt}^{3+} - X^- \dots$, which is referred to as the charge-density-wave (CDW) state. $\text{Pt}_2(\text{dta})_4\text{I}$ exhibits a distinct ground state with metal-sublattice dimerization [24]: $\dots \text{I}^- \dots \text{Pt}^{2+} \text{Pt}^{3+} - \text{I}^- - \text{Pt}^{3+} \text{Pt}^{2+} \dots \text{I}^- \dots$, which is referred to as the alternate charge-polarization (ACP) state. $\text{Ni}_2(\text{dta})_4\text{I}$ is a Mott insulator [25] and has a mono-valent ground state without any lattice distortion. These ground states can be tuned by pressure [26–30] as well as by replacing the bridging halogens [23,31], counter ions [29,32,33] and ligand molecules [34].

Topological excitations of such competing ground states must provide rich physics. Soliton [35] and polaron [36] solutions have indeed been found for an *MMX* Hamiltonian of the Su-Schrieffer-Heeger type [37], and an analogy between *MMX* chains and *trans*-polyacetylene has been pointed out. The solitons turned out to have lower formation energies and smaller effective masses than the polarons. The direct $M(d_{z^2})$ - $M(d_{z^2})$ overlap effectively reduces the on-site Coulomb repulsion,

and therefore, electrons can be more itinerant in *MMX* chains. In fact *MMX* chains exhibit a much higher room-temperature conductivity than *MX* chains [38]. Then we take more and more interest in solitons as charge or spin carriers. Thus motivated, we study the optical conductivity of *MMX* solitons with particular emphasis on a comparison between the *pop* and *dta* complexes. *MMX* uniform absorption spectra have recently been investigated [39], but photoinduced ones, which are supposed to serve as prominent probes for nonlinear excitations, have neither measured nor calculated yet. Let us start exploring photoexcited mixed-valent binuclear metal complexes.

We describe *MMX* chains in terms of the one-dimensional $\frac{3}{4}$ -filled single-band Peierls-Hubbard Hamiltonian

$$\begin{aligned} \mathcal{H} = & -t_{MM} \sum_{n,s} (b_{n,s}^\dagger a_{n,s} + a_{n,s}^\dagger b_{n,s}) \\ & - \sum_{n,s} [t_{MXM} - \alpha(v_{n+1} - v_n)] (a_{n+1,s}^\dagger b_{n,s} + b_{n,s}^\dagger a_{n+1,s}) \\ & - \beta \sum_{n,s} [(v_n - u_{n-1})n_{n,s} + (u_n - v_n)m_{n,s}] \\ & + U_M \sum_n (n_{n,+}n_{n,-} + m_{n,+}m_{n,-}) \\ & + V_{MM} \sum_{n,s,s'} n_{n,s}m_{n,s'} + V_{MXM} \sum_{n,s,s'} n_{n+1,s}m_{n,s'} \\ & + \frac{K_{MX}}{2} \sum_n [(u_n - v_n)^2 + (v_n - u_{n-1})^2], \end{aligned} \quad (1)$$

where $n_{n,s} = a_{n,s}^\dagger a_{n,s}$ and $m_{n,s} = b_{n,s}^\dagger b_{n,s}$ with $a_{n,s}^\dagger$ and $b_{n,s}^\dagger$ being the creation operators of an electron with spin $s = \pm$ (up and down) for the $M d_{z^2}$ orbitals in the n th *MMX* unit. t_{MM} and t_{MXM} describe the intradimer and interdimer electron hoppings, respectively. α and β are the intersite and intrasite electron-lattice coupling constants, respectively, with K_{MX} being the metal-halogen spring constant. u_n and v_n are, respectively, the chain-direction displacements of the halogen and metal dimer in the n th *MMX* unit from their equilibrium positions. We assume, based on the thus-far reported experimental

observations, that every M_2 moiety is not deformed. We set t_{MXM} and K_{MX} both equal to unity in the following.

Here, we focus our research on platinum complexes with mixed-valent ground states. The intradimer transfer integral and Coulomb interactions are, unless otherwise noted, set for $t_{MM} = 2.0$, $U_M = 1.0$, $V_{MM} = 0.5$, $V_{MXM} = 0.3$. The Coulomb repulsion is much weaker on platinum

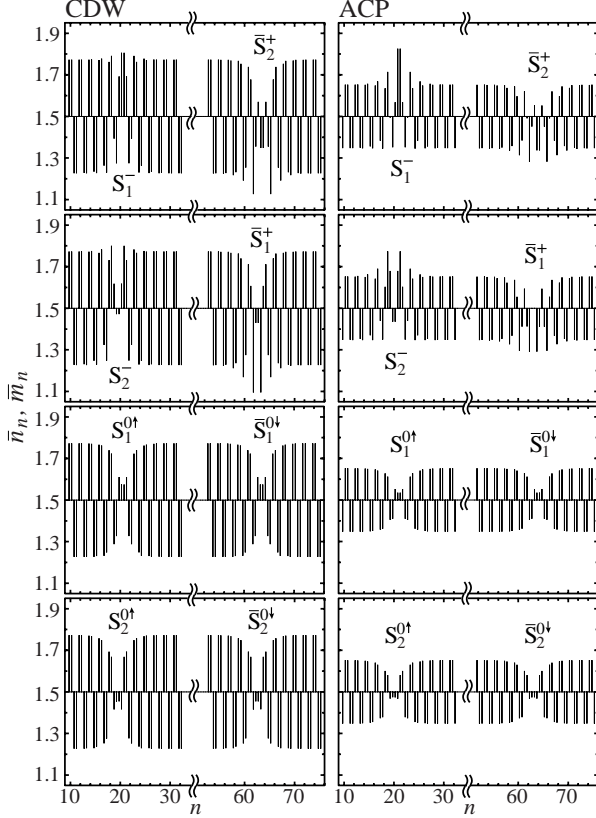


FIG. 1. Spatial configurations of the stable soliton-antisoliton pairs on the CDW and ACP backgrounds, where quantum averages of the local electron densities, $\sum_s \langle a_{n,s}^\dagger a_{n,s} \rangle \equiv \bar{n}_n$ and $\sum_s \langle b_{n,s}^\dagger b_{n,s} \rangle \equiv \bar{m}_n$, are measured in comparison with the average occupancy.

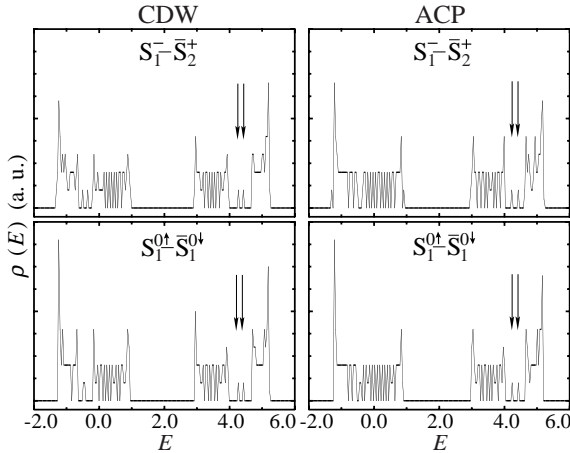


FIG. 2. Density of states for the optimum soliton-antisoliton pairs on the CDW and ACP backgrounds.

ions than on nickel ions. The electron-lattice coupling constants are taken in two ways as $\alpha = 0.0, \beta = 1.4$ and $\alpha = 0.3, \beta = 1.0$, which are relevant to the pop and dta complexes and indeed give the CDW and ACP ground states, respectively, under the above parametrization. The lattice distortion is adiabatically determined at each temperature so as to minimize the free energy, where the chain length is kept unchanged.

The optical spectra are obtained by calculating the matrix elements between the ground state $|g\rangle$ of energy E_g and the excited states $|l\rangle$ of energy E_l ($l = 1, 2, \dots$) for the current operator $\mathcal{J} = \sum_{n=1}^N \sum_{s=\pm} j_{n,s}$ with

$$j_{n,s} = \frac{ie}{\hbar} c_{MM} t_{MM} (b_{n,s}^\dagger a_{n,s} - a_{n,s}^\dagger b_{n,s}) + \frac{ie}{\hbar} c_{MXM} \times [t_{MXM} - \alpha(v_{n+1} - v_n)] (a_{n+1,s}^\dagger b_{n,s} - b_{n,s}^\dagger a_{n+1,s}), \quad (2)$$

where c_{MM} and c_{MXM} are the average M - M and M - X - M distances, respectively, and are set for $c_{MXM} = 2c_{MM}$. The real part of the optical conductivity is given by

$$\sigma(\omega) = \frac{\pi}{N\omega} \sum_l |\langle l | \mathcal{J} | g \rangle|^2 \delta(E_l - E_g - \hbar\omega). \quad (3)$$

$|g\rangle$ is set for the Hartree-Fock (HF) ground state, while $|l\rangle$ is calculated within and beyond the HF approximation, being generally defined as

$$|l\rangle = \sum_s \sum_{\epsilon_\mu \leq \epsilon_F} \sum_{\epsilon_\nu > \epsilon_F} f(\mu, \nu, s; l) c_{\nu,s}^\dagger c_{\mu,s} |g\rangle, \quad (4)$$

where ϵ_F is the Fermi energy and $c_{\lambda,s}^\dagger$ creates an electron with spin s for the λ th HF eigenstate with an eigenvalue ϵ_λ . At the HF level, any excited state is simply approximated by a single Slater determinant as $f(\mu, \nu, s; l) = \delta_{\mu\nu s, l}$. In order to take account of the excitonic effect, we further consider excited states of the configuration-interaction (CI) type, where $f(\mu, \nu, s; l)$ is determined so as to diagonalize the original Hamiltonian (1). We set N , the number of unit cells, equal to 84, which results in spending 2 GB memory on the CI calculation.

Photogenerated defects are necessarily in pairs. We visualize the convergent soliton (S)-antisoliton (\bar{S}) pairs in Fig. 1, which have been calculated at a sufficiently low temperature $k_B T/t_{MXM} = 10^{-3}$ without any assumption on their shapes in an attempt to elucidate the intrinsic excitation mechanism. S_1 and S_2 designate the lowest- and highest-energy soliton solutions, both of which lay their centers on halogen sites (metal dimers) with the CDW (ACP) background. There are further soliton solutions with intermediate energies, but they are unstable in pairs.

Such a pair of solitons generally gives two additional levels within the gap, which are indicated by arrows in Fig. 2. The lower one is doubly filled, while the upper one is vacant. There appear further soliton-related mid-gap

levels in the strong-coupling and/or -correlation region [40–42]. These levels are all localized around the soliton centers [35]. In Fig. 2, the lower and upper ones are assigned to S^- and S^+ , respectively, in the case of charged soliton pairs, whereas both the levels originate from a single S^0 itself in the case of neutral soliton pairs because of the breakdown of the spin up-down symmetry. The intragap soliton levels are plotted as functions of the Coulomb interaction in Fig. 3. The Coulomb effect distinguishes charged soliton pairs $S^- - \bar{S}^+$ from singly excited charged solitons S^\pm . Without any Coulomb interaction, the two localized levels of $S^- - \bar{S}^+$ are essentially the same as those of single S^\pm . In the case of the CDW background, with increasing Coulomb interaction, the levels of S^- and S^+ move upward and downward, respectively, and then cross. For further increasing Coulomb interaction, the doubly occupied S^- level goes higher in energy than the vacant S^+ level, provided that they are singly excited. Therefore, in such a strong correlation regime, S^- and S^+ are restructured in a pair so as to have lower- and higher-lying levels, respectively, where the pair-creation energy $\Delta E(S^- - \bar{S}^+)$ is smaller than twice the single-excitation energy $2\Delta E(S^\pm)$. Hence, $\Delta E(S^- - \bar{S}^+)$ jumps at certain Coulomb-interaction values, as shown in Fig. 4. Since the same scenario applies in the case of increasing Peierls coupling α , $S^- - \bar{S}^+$ and single S^\pm behave differently on the ACP background lying in the large- α region, regardless of Coulomb interaction. Thus, photoinduced and doping-induced charged solitons should exhibit distinct absorption spectra in general. This is not the case with neutral solitons. The level structure, formation energy and absorption spectrum of any photoinduced $S^{0\uparrow} - \bar{S}^{0\downarrow}$ can be obtained by superposing those of singly excited $S^{0\uparrow}$ and $S^{0\downarrow}$. Photoinduced and chemical-defect-induced neutral-soliton absorption spectra may essentially be the same.

Another Coulomb effect causes a striking contrast between the CDW and ACP solitons. With increasing Coulomb interaction, the intragap soliton levels generally move away from the gap center. Since the electron-hole symmetry is broken in the Hamiltonian (1), soliton-related electron and hole levels may be asymmetric with respect to the center of the gap. It is indeed the case with the CDW background, while on the ACP background, a soliton of charge σ , S^σ , and that of spin s , S^{0s} , described in terms of electrons are still almost equivalent to their counterparts $S^{-\sigma}$ and S^{0-s} described in terms of holes, respectively. In consequence, *photoinduced soliton absorption spectra for the pop complexes should split into two bands, while those for $Pt_2(dta)_4I$ should consist of a single band*, as demonstrated in Fig. 5. In mixed-valent MX chains, neutral solitons seem to be the lowest-energy pair excitations [43]. Photoexcited $[Pt(en)_2X](ClO_4)_2$ ($X = Cl, Br$; $en = \text{ethylenediamine} = C_2H_8N_2$) [44,45] indeed exhibit mid-gap absorption attributable to neutral solitons. In mixed-valent MMX chains, on the other hand, charged solitons may be the lowest-energy excita-

tions because the on-site Coulomb repulsion U_M and the Holstein coupling β are effectively smaller and larger, respectively [17,24]. Polarons have much higher formation energies for both MX [1,43] and MMX [36] chains and can therefore be generated from relatively high-energy excited states corresponding to the electron-hole continuum [9,10]. An excitation energy close to the Peierls gap directly induces charge-transfer excitons [8] and they may relax into soliton pairs in nonradiative channels for MMX chains as well. Then there arises an interesting issue: charged solitons or neutral solitons? The optical conductivity spectra possibly answer this question. For the pop complexes, charged (neutral)-soliton mid-gap absorption spectra are double-peaked and the higher (lower)-energy band has a larger oscillator strength, where the excitonic effect is essential. As for $Pt_2(dta)_4I$, further experiments such as electron-spin-resonance measurements [46] are supplementary to distinguish between charged and neutral solitons.

The doublet structure of soliton-induced spectra is characteristic of MMX chains and is a consequence of *the broken electron-hole symmetry and effective Coulomb correlation* [47]. Indeed MX chains also lose the electron-hole

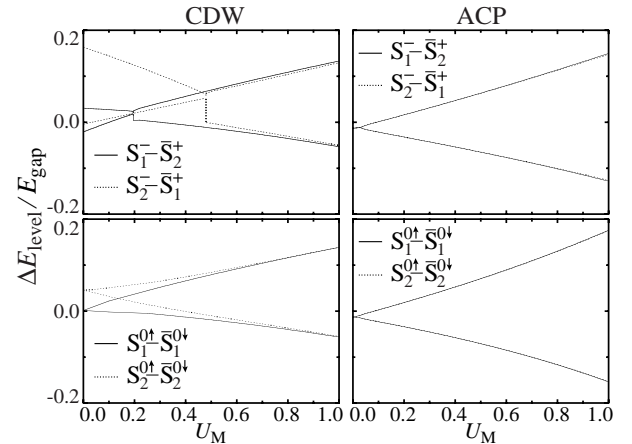


FIG. 3. Energy shifts of the localized levels accompanying the stable soliton-antisoliton pairs on the CDW and ACP backgrounds, which are measured from the gap center and scaled by the Peierls gap, as functions of the Coulomb interaction, where U_M varies keeping the relation $U_M = V_{MM}/0.5 = V_{MXM}/0.3$.

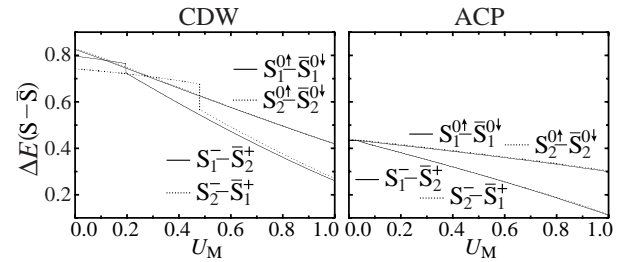


FIG. 4. Formation energies of the stable soliton-antisoliton pairs on the CDW and ACP backgrounds as functions of the Coulomb interaction, where U_M varies keeping the relation $U_M = V_{MM}/0.5 = V_{MXM}/0.3$.

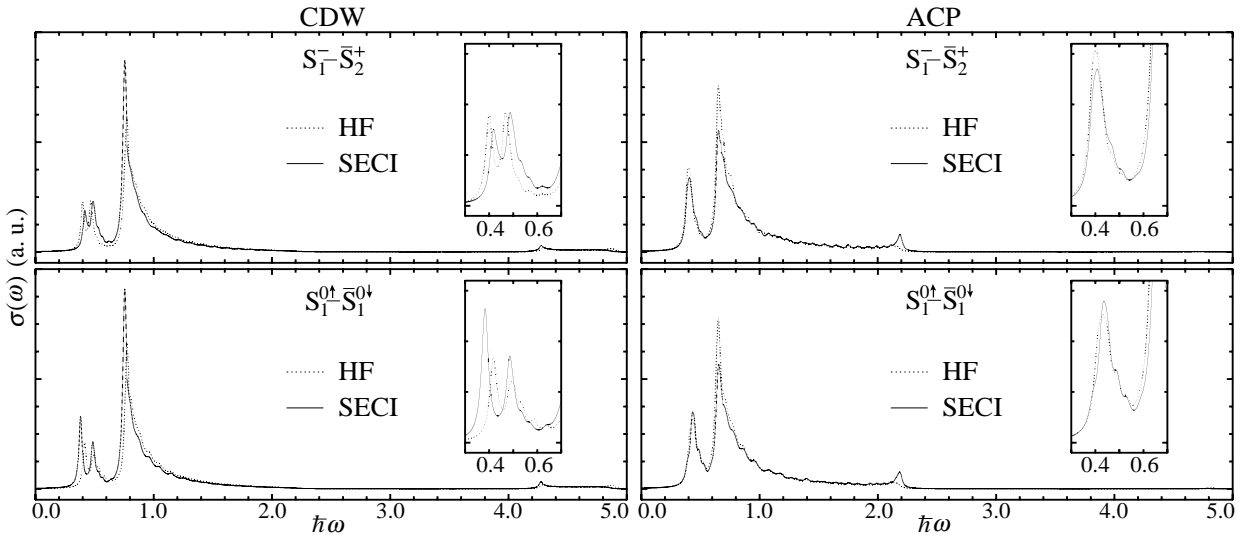


FIG. 5. Hartree-Fock (HF) and single-excitation configuration-interaction (SECI) calculations of the optical conductivity spectra for the optimum soliton-antisoliton pairs on the CDW and ACP backgrounds, where each line has been Lorentzian-broadened. Mid-gap absorption bands due to solitons are scaled up in insets.

symmetry with their $X p_z$ electrons activated [17,48], but it is not the case with the PtX compounds, where the energy level of the $X p_z$ orbitals is much lower than that of the $M d_{z^2}$ orbitals, and thus, the p -orbital contribution may effectively be incorporated into the intermetal super-transfer energy of a single-band Hamiltonian of the eq. (1) type. In fact, the photoexcited $[\text{Pt}(\text{en})_2\text{I}](\text{ClO}_4)_2$ [49] and $[\text{Pt}(\text{en})_2\text{Br}](\text{ClO}_4)_2$ [45] yield single-peaked mid-gap absorption spectra attributable to charged and neutral solitons, respectively, though the latter S^0 spectrum is accompanied by a weak shoulder [50]. Figure 5 demonstrates that a breakdown of the electron-hole symmetry does not necessarily lead to the doublet structure. The double-peaked soliton absorption is peculiar to the pop complexes but missing in $\text{Pt}_2(\text{dta})_4\text{I}$. Observations of such a contrast will strongly support effective Peierls coupling in $\text{Pt}_2(\text{dta})_4\text{I}$. Distinguishable observations of charged and neutral solitons in the pop complexes will contribute toward realizing photoswitched charge or spin conduction. Photoinduced infrared absorption measurements on MMX compounds are strongly encouraged.

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